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Extraction or Destruction of Chemical Pollutants from Aqueous Waste Streams

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A toluene diamine wastewater was found treatable with benzene.

In all these wastes there are unextractable fractions.

Attempts were made to treat glycol, toluene diamine and light chlorinated hydrocarbon wastewaters with ozone, but results were not satisfactory.

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EXTRACTION OR DESTRUCTION OF CHEMICAL POLLUTANTS FROM AQUEOUS WASTE STREAMS

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FOREWORD

The Environmental Protection Agency was established to coordinate administration of the major Federal programs designed to protect the quality of our environment.

An important part of the agency's effort involves the search for information about environmental problems, management techniques and new technologies through which optimum use of the nation's land and water resources can be assured and the threat pollution poses to the welfare of the American people can be minimized.

EPA's Office of Research and Development conducts this search through a nationwide network of research facilities.

As one of these facilities, the Robert S. Kerr Environmental Research Laboratory is responsible for the management of programs to: (a) investigate the nature, transport, fate and management of pollutants in groundwater; (b) develop and demonstrate methods for treating wastewaters with soil and other natural systems; (c) develop and demonstrate pollution control technologies for irrigation return flows; (d) develop and demonstrate pollution control technologies for animal production wastes; (e) develop and demonstrate technologies to prevent, control or abate pollution from the petroleum refining and petrochemical industries, and (f) develop and demonstrate technologies to manage pollution resulting from combinations of industrial wastewaters or industrial/municipal wastewaters.

This report contributes to the knowledge essential if the EPA is to meet the requirements of environmental laws that it establish and enforce pollution control standards which are reasonable, cost effective and provide adequate protection for the American public.

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Director
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Research Laboratory

ABSTRACT

The use of solvent extraction and ozonation to treat various industrial waste waters was studied. Most were light chlorinated hydrocarbon, solvent wastes and were principally extracted with a high molecular weight paraffin petroleum fraction. Distribution data on related pure chlorinated compounds were also obtained. The economics of solvent extraction versus steam stripping was examined. Though chlorinated solvents can be effectively removed by extraction, stripping appears to be more economical.

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LIST OF ABBREVIATIONS AND SYMBOLS

ABBREVIATIONS

atm	-- atmosphere
Btu	-- British thermal unit
EDC	-- ethylene dichloride
COD	-- chemical oxygen demand
FRC	-- flow recording controller
GPM	-- gallons per minute
H.E.T.P.	-- height equivalent to a theoretical plate
ℓ	-- liter
mil eq	-- mili equivalent
mgm	-- miligram
PG	-- propylene glycol
ppm	-- parts per million
TDA	-- toluene diamine
TOC	-- total organic carbon
TRC	-- temperature recording controller

SYMBOLS

A	-- area, ft^2
D	-- diameter, ft
E	-- extraction factor, K Lo/Lw
H	-- Henry's law constant, atm
ΔH_v	-- latent heat of vaporization
K	-- equilibrium constant, Y / X or Xo/Xw
L	-- liquid flow rate, moles per unit time
N	-- number of theoretical stages or transfer units
p	-- partial pressure, atm
p*	-- vapor pressure, atm
Q	-- heat flow, Btu/hr
S	-- stripping factor, KV/L
t	-- temperature °F
Δt	-- temperature difference, °F
U	-- heat transfer coefficient, BTu/hr-ft^2-°F
V	-- vapor flow rate, moles per unit time
V_1, V_2	-- molar volumes
X	-- liquid mole fraction
Y	-- vapor mole fraction

greek

γ -- activity coefficient
δ -- Hildebrand's solubility parameter
π -- total pressure, atm

subscripts

E -- in extractor
g -- gas phase
L -- liquid phase
o -- oil stripper or oil phase
Sat -- at saturation
v -- volume basis
w -- water stripper or water phase

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SECTION 1

INTRODUCTION

It is not the intention of this report to present a study of solvent extraction as a unit operation. This has been done in many books and articles (1-4).

Similarly, for background information about the ozonation work, the reader is referred to two recent papers by the Principal Investigator (5, 6).

The work described in this report is an attempt to apply the above two methods, often lumped with others under the heading physical-chemical treatment, to improve the quality of certain specific waste waters. This work was done in cooperation with the state of Louisiana, with Gulf South Research Institute (GSRI) of Baton Rouge and with several chemical companies in Louisiana and with the Environmental Protection Agency's Robert S. Kerr Environmental Research Laboratory of Ada, Oklahoma. Physical-chemical methods are generally used when biological treatment is for some reason inadequate, or to assist biological treatment by the prior removal of refractory and toxic compounds, or the post removal of traces of undesirable constituents.

Solvent extraction is best compared with other physical methods which actually remove certain substances from solution. The methods to which it is most analogous and with which it must often compete are stripping and adsorption. Each of these methods relies on a selective transfer between phases - stripping by a favorable relative volability, extraction by a favorable relative solubility, and adsorption, of course, by a favorable adsorption equilibrium. Each of these methods offers the possibility of recovery of the solute which, in some cases, can significantly effect the economics of treatment.

Very little use has been made of solvent extraction in waste water treatment. The only common process is the recovery of phenolic substances. For years phenol has been recovered from coke oven liquor with an aromatic oil. More recently the Phenex (Exxon) process has been developed which uses a light catalytic oil to extract phenol from refinery wastes. Other solvents have been reported which give better distribution ratios (7, 8). In recent reviews or symposiums on water reuse almost no mention is made of solvent extraction.

Solvent extraction processes can be categorized as follows:

1. Extraction of a solute having reasonable volatility into a nonvolatile-water immiscible solvent.

2. Extraction of a nonvolatile solute into a volatile immiscible solvent.

3. Cases 1 and 2 with a partially miscible solvent.

4. Extraction of a chemically reactive solute.

5. Extraction of water plus a valuable solute to produce a water more concentrated in other components, followed by recovery of the solute from water.

6. Extraction of water from a waste to produce a concentrated waste which can be burned or otherwise disposed of. Pure water can be recovered also.

In this work we will be concerned with the first three categories. Partial miscibility of solvent and water means that there must also be a solvent recovery step from the water, usually by steam stripping. The category of nonvolatile solvent and volatile solute is most economical as a rule, because of lower solvent recovery heat consumption.

Ozonation has been used for years in Europe, particularly to purify drinking water. Research has shown that BOD and COD can be reduced by ozonation. Recent work on ozone decomposition kinetics in water (5) and on the removal of organics from waste water (6) has clarified the mechanism of ozone reduction of organic content and has demonstrated that high utilization efficiencies can be obtained.

SECTION 2

CONCLUSIONS

1. Many light Chlorinated hydrocarbon solvents (1-3 carbon atoms) can be effectively extracted from industrial wastes.

2. In most instances the same substances can be steam stripped from the wastes with lower cost.

3. Solvent extraction is likely to compete with stripping when the water solubility is higher and the volatility lower than usually encountered in light chlorinated hydrocarbon wastes.

4. Toluene diamine can be extracted with benzene and the benzene plus other volatile constituents can be steam stripped from the water.

5. After extraction with C_{12-13} paraffin solvents, wastewaters in these classes generally contained unidentified nonextractables ranging up to 500 ppm. These nonextractables may have included oxygenated compounds.

6. Ozone is not effective in treating glycol wastes.

7. Ozone is not effective at TOC (Total Organic Carbon) levels of several hundred.

8. Ozone removes color and odor very much more rapidly than it removes TOC.

9. Ozone is generally effective in removing color.

10. At a given ozone level, the rate of reaction with organics is proportional to the organic level. Even though the cost of treatment with ozone decreases with decreasing organic load, the efficiency of ozone utilization also decreases.

11. As ozone has a short life, it is very important that proper contact be made between the gas and the waste water.

SECTION 3

RECOMMENDATIONS

The chlorinated wastes considered in this study should be treated by stripping rather than extraction if only chlorinated hydrocarbons are to be removed. However, the large amounts of material not extracted by paraffin oil or benzene should be identified, and perhaps slightly miscible but volatile solvents examined. Extraction should be considered in treating the toluene diamine waste.

Dual Solvent systems should be studied in an effort to determine more efficient and more flexible extraction systems.

Ozone contacting systems should be studied in more detail with particular attention to the gas-liquid, gas solid, and solid liquid interfaces. The effects of these interfacial interactions on the chemical kinetics of both ozone decomposition and the subsequent reaction with organics should be studied.

Ozonation should not be used as a primary treatment for highly contaminated wastes. Ozone has always been envisioned as a tertiary treatment to polish wastes where treatment is less than adequate by other methods.

SECTION 4

DISTRIBUTION COEFFICIENTS FOR PURE COMPONENTS

A high percentage of the industrial waste streams studied in this research program contain chlorinated hydrocarbons with EDC (1,2-dichloroethane) being of principal concern. Though the waste streams are a complex mixture containing unidentified components, some of which cannot be extracted, it was felt that data on some pure components would be helpful. Since some of the waste streams are quite acidic, data were also obtained in 15% HCl, which as expected, had some effect on the results

The data are given in TABLE 1. These data are for screening purposes and are not of high precision. To save time only the water phase was analyzed, but the data are sufficient to show trends. Generally with distribution coefficients as high as these, the precise value is of less significance because the size of the extractor will increase only slightly with decreasing distribution; and solvent recovery cost is independent of the distribution except as it affects solvent rate which is already small.

Generally, the extraction data were obtained by agitating the water samples with the solvent sufficiently to obtain equilibrium. The phases were separated and the water phase was analyzed by the total organic carbon analyzer or the gas chromatograph.

From the data given in TABLE 2 several points may be noted. As would be expected, the distribution coefficient increases with decreasing solubility in water and decreasing Hildebrand solubility parameter. The coefficient increases, generally, with chlorine content and with asymmetry in chlorine distrubution; i.e., 1,1,1-trichloroethane is greater than 1,1,2-trichloroethane. Unsaturation increases the distribution coefficient.

TABLE 1. PURE COMPONENT DISTRUBUTION DATA

Solvent Water = 1/10
Concentration in mgm/l

Compound	Water feed	Water phase	Oil phase	Distribution K_{vL}
Methylene chloride	1,510	888	6,220	7
	1,705*	687	10,200	15
	170*	66	1,040	16
Chloroform	8,000	1,096	69,000	63
	6,000	1,176	48,200	41
	2,000	272	17,300	64
	1,120	118	10,000	85
	600	109	4,900	45
Carbon tetrachloride	680	0	--	> 100
	68	0	--	> 100
Ethylene dichloride (EDC)	8,700	3,340	53,600	16
	4,350	1,397	29,500	21
	1,305	469	8,400	18
	820	230	6,900	30
	82	20	620	31
	7,013*	1,450	55,600	38
	721*	176	5,450	31
	70*	16	540	34
	6,992*	2,750	42,350	16
	703*	260	4,400	17
15% HCl	70*	45	250	5.5
1,1,1-Trichloroethane	1,000	78	9,200	118
	300	0	--	--
1,1,2-Trichloroethane	2,800	582	22,200	38
	1,492	292	12,000	41
	746	152	5,400	39
	280	73	2,100	28
	4,028	446	35,800	80
	802*	143	6,590	46

TABLE 1 (continued)

1,1,2-Trichloroethane 15% HCl	882*	270	6,120	23
1,1,2,2-Tetrachloroethane	2,620	475	15,500	33
	1,279	346	9,300	27
	640	156	4,800	31
	202	50	1,500	30
1,2-Dichloroethane (CIS)	378	62	3,200	51
	189	27	1,600	60
	95	16	785	49
Trichloroethylene	860	129	7,300	57
	646	52	5,900	114
	86	0		
Tetrachloroethylene	372	0		> 100
	37	0		> 100
Benzene	1,092*	66	10,300	150

*Analysis by TOC

TABLE 2. CHLORINATED SOLVENT DATA

	Distribution Coefficient K_{vL}	Density $(\frac{gm}{cm^3})$	Sol. H_2O (wt. fraction)	Sol. parameter	B.P. °C
CH_2Cl_2	7-16	1.33	.02	9.8	40
$CHCl_3$	60	1.484	.0073	9.2	61-62
CCl_4	>100	1.589	.0008	8.6	132-134
$1,2\text{-}C_2H_4Cl_2$	20-30	1.246	.009	9.9	83-84
$1,1,1\text{-}C_2H_3Cl_3$	>100			8.5	74.1
$1,1,2\text{-}C_2H_3Cl_3$	40				113-114
$1,1,2,2\text{-}C_2H_2Cl_4$	30	1.587	.0028		146.5
$1,2\text{-}C_2H_2Cl_2$(CIS)	50			9.1	60
C_2HCl_3	60-100				86.7
C_2Cl_4	>100		10^{-4}	9.3	121

SECTION 5

EXTRACTION DATA ON WASTE STREAMS

The results of extracting various industrial wastes with a paraffinic petroleum oil having approximately the properties of tridecane plus a few data using benzene as solvent are shown in TABLE 3. Except for the last data with a toluene diamine waste, the ratio of solvent to water was one to ten. The results are confusing and sometimes contradictory. This probably results from sample variability and the fact that large amounts of non-extractables are in most wastes. These nonextractables are not chlorinated hydrocarbons such as were investigated in the previous section. Part of the difficulty also results from the lack of correlation between TOC (Total Organic Carbon) and chromatograph analysis.

In order to obtain some meaning from these results we have assumed that the TOC can be divided into two parts: the first part is extracted at constant distribution coefficient while the second part is not extracted at all. For that part that is extracted, the concentration remaining after each extraction will plot as a straight line on semilog paper since each extraction removes a constant percent of the remaining extractables. Therefore, by trial and error, a number is found which when subtracted from all the TOC values causes the remainder to plot in a line, Figure 1-3. The data in Fig. 1 only involve three points and the results do not constitute a proof of the assumption. For any three points, x, y,z, if $x > y > z$ and $(x-y) > (y-z)$. Then a constant can be found to satisfy the relation $\log (x-c)/(y-c) = \log (y-c)/(z-c)$ which gives the desired straight line. The data in Figure 2 with five extractions is a better confirmation of the assumption. The data in Figure 1 are plotted without regard to the magnitude of the ordinate to show slopes only since the same slope indicates the same distribution coefficient.

We will begin with sample 011A which is principally a high pH EDC waste. The plot in Figure 1 gives a slope completely different from pure EDC and most other EDC wastes, in spite of the fact that EDC analysis indicated that nearly all the EDC was extracted. The final entry in TABLE 3 for 011A was an attempt to remove all the extractables. All the EDC was removed, but the TOC data are contradictory and completely inconsistent with the EDC data. For instance, over 3000 ppm of EDC was measured as against 350-550 ppm of TOC, and the complete removal of the EDC only dropped the TOC by 200 ppm.

Sample 011B, also a high EDC waste, but acid instead of alkaline as was 011A, showed similar extraction characteristics with a large quantity of unidentified nonextractables.

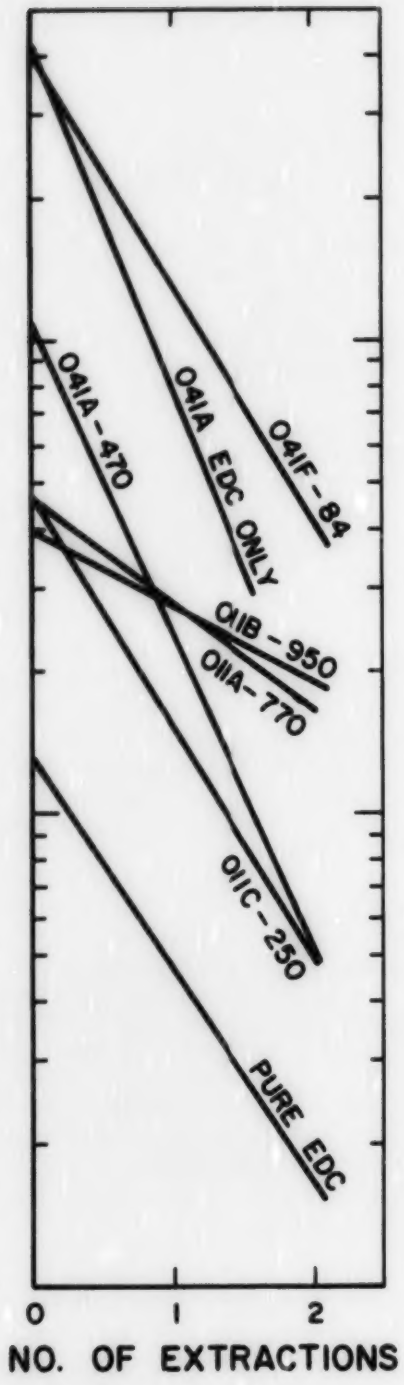

Figure 1. Comparative extraction coefficients for various industrial waste streams

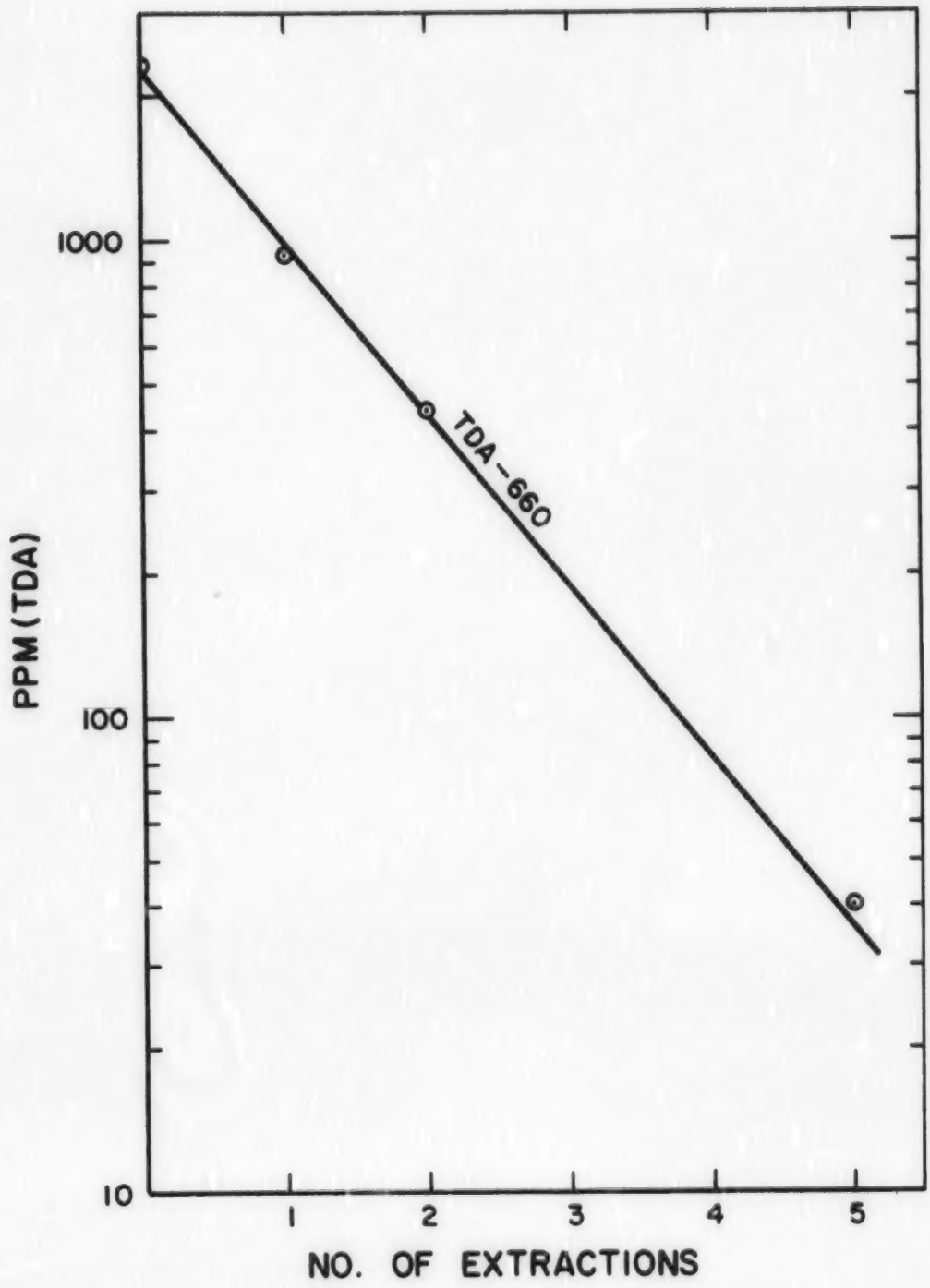

Figure 2. Extraction of toluene diamine.

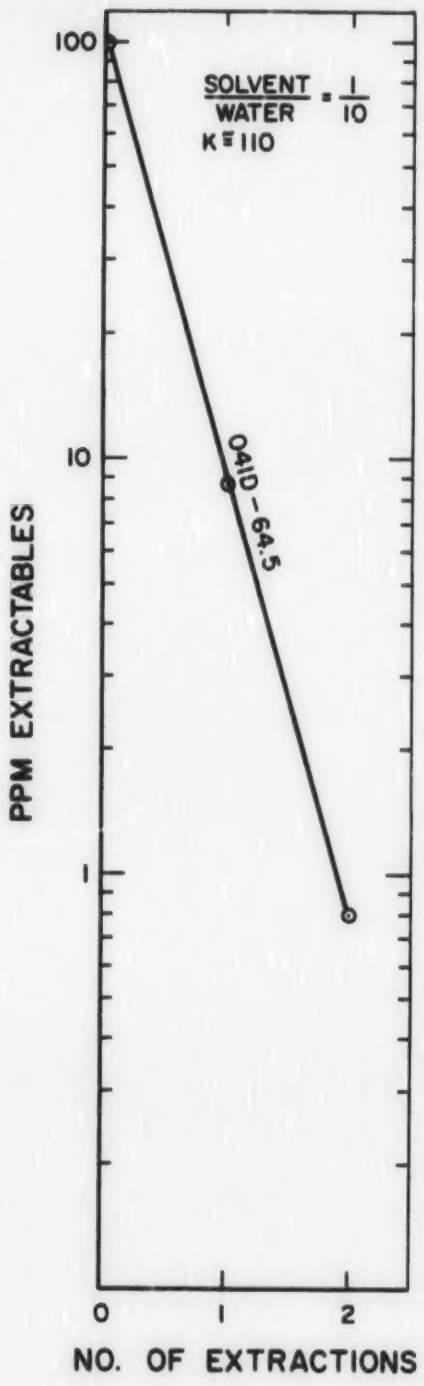

Figure 3. Extraction of aromatic waste

Sample 011C, reported to be principally EDC plus some methyl chloride (which would have been lost) is an alkaline sample but less so than 011A. Figure 1 indicates that the extractables behave much as EDC in sharp constrast to 011A. Sample 041A, another alkaline sample high in EDC, shows TOC removal even more rapid that 011C. The data on EDC removal obtained by GC (Gas Chromatography) rather than TOC typically show an even more rapid removal than pure EDC as measured by TOC. Sample 041C(acid) shows a much lower TOC than indicated by COD analysis, but is consistent with the chemical analysis, which shows only small amounts of chlorinated solvents.

Sample 041D (ph $\tilde{=}$ 7) contains aromatic constituents as well as EDC. A plot of this waste is shown in Figure 3, and we see that all but 64 ppm of the TOC is extracted at a very high rate.

Sample 041F (pH >7) a chlorinated waste of fairly low TOC, shows a very rapid extraction of about a third of the TOC.

Our analysis of sample 081A (pH > 7) shows a low TOC about half of which can be extracted. Samples 081B(acid) and 081C(basic) shows very rapid extraction of about two thirds of the TOC. These samples are interesting in that 081B is very acid and 081C is very alkaline, but both show greater removal of the extractables than obtained with pure EDC.

Sample 131A showed almost no extractables. Our analysis of sample 161A(pH$\tilde{=}$7) showed a low TOC in contrast to a GSRI COD of about 100 ppm. Sample 161B is an acid EDC containing stream with very rapid removal of nearly half of the TOC. Sample 161C is a very acidic stream, supposedly containing appreciable EDC and other chlorinated solvents, but our data show almost no removal of the very high TOC.

Sample 221A is another highly acidic stream containing a high EDC content. This sample shows very rapid removal of about 300 ppm TOC, but over 2000 ppm of nonextractables remain. Sample 221B, an alkaline high EDC waste, shows TOC removal very similar to the highly acidic 221A. Again we found a very high level of nonextractables. Sample 221C, with a high TOC but low chlorinated solvent content, shows very little extractable content.

The final sample contains a high level of toluene diamine. Figure 2 shows that about 2750 ppm of TOC can be extracted by benzene with a distribution coefficient of a little over one.

TABLE 3. EXTRACTION OF INDUSTRIAL SAMPLES
Solvent/Water=1/10

25°C

Concentrations in mgm/l

Sample No. and (analytical parameter)	Waste Type	Water feed	Water phase	No. of extractions
011A(TOC)	EDC	1,233	1,057	1
			934	2
011A(EDC)	EDC	3,964	1,020	1
			106	2
011A (Extracted with Benzene 4 times and oil 3 times)				
		3,643(EDC)	9	
		3,292(EDC)	0	
		355(TOC)	79	
		522(TOC)	312	
011B(TOC)	EDC	1,355	1,224	1
			1,144	2
011C(TOC)	EDC	817	403	1
			301	2
041A(TOC)	EDC	1,545	714	1
			522	2
041A(EDC)	EDC	4,270	739	1
			277	2
041C(TOC)	EDC+Arom.	25	21	1
			19	2
041D(TOC)	EDC+Arom.	171	73.2	1
			65.3	2

TABLE 3 (continued)

041F(TOC)	methyl chloride	124	97	1
			88	2
081A(TOC)	tri + tetra chlorohydrocarbons	35.0	24	1
			20	2
		25.0	10	1
		29	15	1
			13	2
081B(TOC)	EDC	82	25	1
			24	2
081B(TOC)	EDC	73	32	1
			31	2
		73	45	1
		68	29	1
081C(TOC)	Tri +Tetra chlorohydrocarbons	92	44	1
		75	35	1
		82	34	1
			34	2
		75	35	1
		94	28	2
			29	1
			27	1
131A(TOC)	Arom.	683	664	1
			641	2
161A(TOC)	EDC	26	21	1
			15	2
161B(TOC)	EDC	254	152	1
			139	2
161C(TOC)	EDC	2,284	2,263	1
			2,247	2
221A(TOC)	EDC	2,384	2,083	1
			2,091	2
221B(TOC)	EDC	2,700	2,405	1
			2,345	2

TABLE 3. (continued)

		2,766	2,394	1
			2,387	2
		2,691	2,346	1
221C	EDC	1,880	1,813	1
			1,797	2
		1,534	1,402	1
			1,394	2
		1,612	1,548	1
Toluenediamine (TOC) Waste - Benzene/Water = 1/1				
		3,000	1,600	1
			1,100	2
			700	5

Section VI

DESIGN OF SOLVENT EXTRACTION PROCESS TO REMOVE CHLORINATED SOLVENTS FROM WASTE WATER

The purpose of this section is to give an approximate design for extracting an idealized waste water to demonstrate general design procedures and probable equipment and utility requirements. The initial concentration of chlorinated solvent in the water was chosen a little below saturation. The final concentration was chosen arbitrarily at a reasonably low value.

The design is based on using a paraffin, highly water insoluble oil to extract the chlorinated hydrocarbons, assumed to be EDC, from the water. A distribution coefficient at the lower end of the range found for the industrial samples was chosen. The EDC is subsequently steam stripped from the oil.

The extractor is an agitated column whose design and power consumption are based on data obtained from du Pont for a process in which dimethyl formamide is extracted from water. As oil and water are immiscible and as the concentration of EDC is low, a constant extraction factor throughout the column may be assumed leading to a very simple calculation of the number of theoretical stages. For a completely stripped solvent, the fraction extracted is $(E^{n+1} - E)/(E^{n+1} - 1)$ in which N is the number of theoretical stages and E is the extraction factor, K·oil rate/water rate.

In the oil stripper there is considerable variation in both the equilibrium constant and the vapor flow rate through the column, so the number of transfer units is calculated using the stripping factor at each end of the tower (Perry's Chemical Engineer's Handbook, 4th edition, p14-29). The height of a transfer unit is based on ranges recommended by U.S. Stonewear.

Arbitrary and safe values were chosen for the oil rate in the extractor and the stripper steam rate. The values are sufficiently small that costs would not be greatly affected by reasonable changes.

EXTRACTOR DESIGN

A sketch of this system is shown in Figure 4. The design bases and calculations follow.

It is assumed that the feed contains 8000 ppm of EDC, and that the product contains 15 ppm EDC.

The distribution coefficient K = Concentration in Oil/Concentration in water, equals 15 on a volume basis. This is a lower value than that of pure EDC but typical of some of the waste streams.

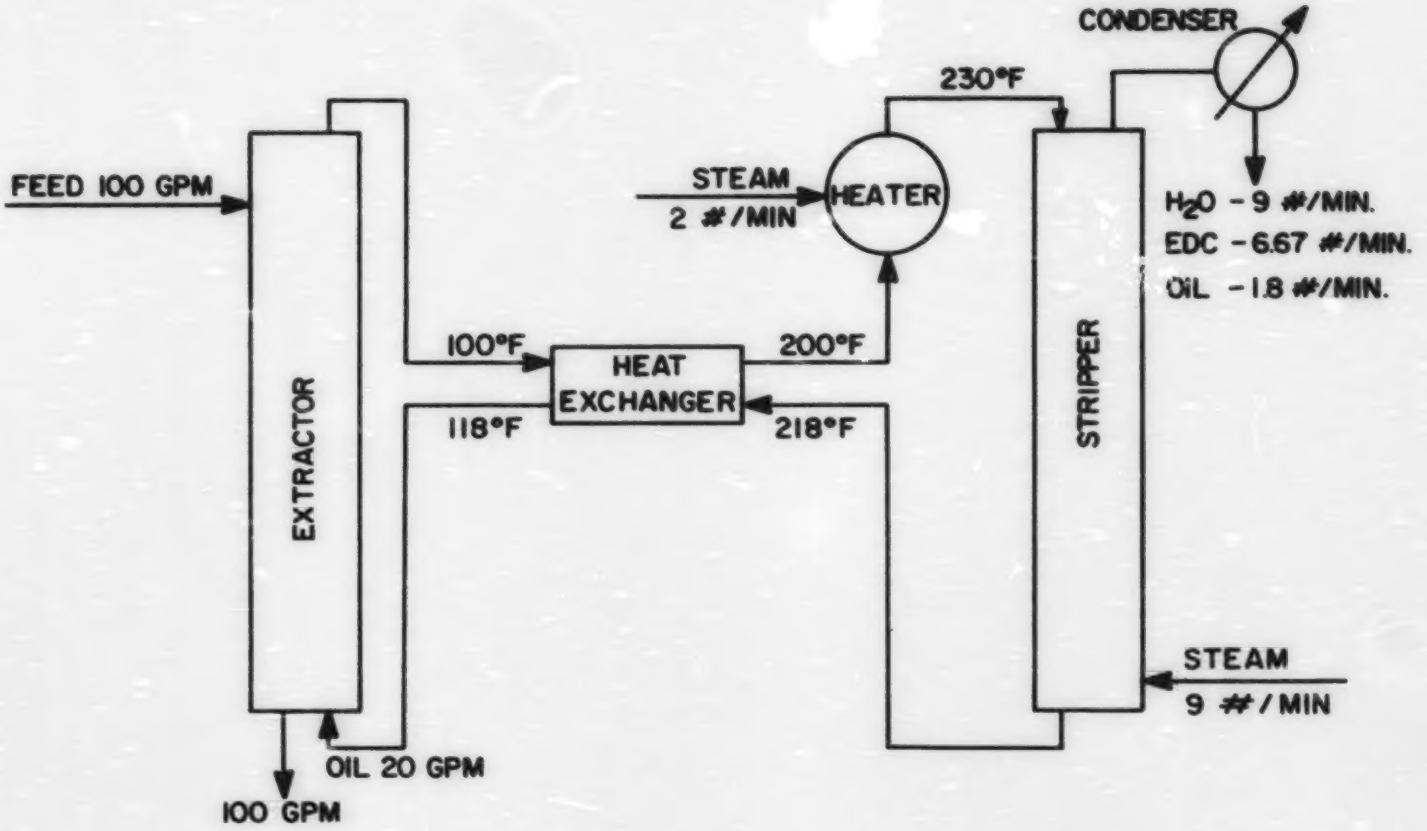

Figure 4. Extraction system.

The volumetric flow ratio of oil/water equal 1/5. Smaller ratios might effect extractor efficiency. The oil is a paraffin hydrocarbon approximated by tridecane. We will assume an agitated column with the following characteristics:

$$\text{H.E.T.P.} = 5\sqrt{D(\text{in})}$$
$$\text{Combined flow} = 300 \text{ gal/hr-ft}^2$$

The extraction factor, $E_v = \frac{\text{oil } xK}{\text{water}} = 3$

With 5.3 stages we have the fraction extracted given by

$$\text{fraction entracted} = \frac{E^{N+1}-E}{E^{N+1}-1} = \frac{3^{6.3}-3}{3^{6.3}-1} = 0.998$$

which is the required recovery, where N is the number of theoretical stages.

Tower diameter is obtained by

$$120 \frac{\text{gal}}{\text{min}} \times \frac{60 \text{ min}}{\text{hr}} \times \frac{1}{300} \frac{\text{ft}^2}{\text{gal/hr}} = 24 \text{ ft}^2$$

$$D = \sqrt{\frac{24 \times 4}{\pi}} \cong 5\ 1/2'$$

Tower height becomes

$$\text{H.E.T.P.} = 5.3\sqrt{5.5 \times 12} = 43"$$

$$H = \frac{40.5 \times 5}{12} = 18, \text{ adding 5' for separation gives 23'.}$$

Power $\cong$ 10 HP

OIL STRIPPER DESIGN

The stripper will be fed at 110°C or 230°F. We will assume that oil and EDC form an ideal mixture. This will be conservative since there is some positive deviation from ideality.

The moles of oil flowing is

$$20 \frac{\text{gal}}{\text{min}} \times (.79 \times 8.33) \frac{\#}{\text{gal}} \times \frac{1}{184\#/\text{mole}} = 0.716 \frac{\text{moles}}{\text{min}}$$

Use a steam rate of 3/2 minimum or 0.50 moles/min, or V = 0.5 x 18 x 60 = 540#/hr.

In stripping this mixture the moles per minute of EDC removed is

$$\frac{100 \times 8.33 \times 8000 \times 10^{-6}}{99} = 0.067 \text{ mol/min}$$

The heat required = 0.067 x 13,600 = 910 Btu/min

This cools the oil,

$$\Delta t = \frac{910 \text{ Btu/min}}{132\frac{\#}{\text{min}} \times .55\frac{\text{Btu}}{\#\text{-°F}}} \cong 12°F$$

Therefore the oil leaves the stripper at 218°F.

At the top of the column

$K_g = 2$

V = .5 moles steam + .067 moles EDC = .567 mole/min

$$S_{TOP} = \frac{VK}{L} = \frac{.567 \times 2}{.716} = 1.58$$

At the bottom of the column

$k_g = 1.55$

$$S_{BOT} = \frac{.5 \times 1.55}{.716 - .067} = 1.2$$

Calculating the number of transfer units with 99.5% recovery gives

$N_{TOP} = 12$

$N_{BOT} = 20$

Assume seventeen transfer units and the height of a transfer unit to be 2 feet, then the column height is 34'. plus 1 foot at each end, or 36'.

Employing the US Stoneware charts for flooding in packed towers and using 1" Intalox saddles we obtain a tower diameter of 1 ft.

HEAT EXCHANGER CALCULATIONS

$$Q = WC_p(t_2 - t_1) = (20 \times 8.33 \times 60 \times .79)\#/\text{hr} \times .51\ \frac{\text{Btu}}{\#\text{-°F}}$$

= 400,000 Btu/hr

U = 75

Δt = 18

$$A = \frac{400,000}{75 \times 18} = 300 \text{ ft}^2$$

OIL HEATER

$$Q = 10{,}000\#/hr \times 30°F \times \frac{.55 Btu}{hr\text{-}ft^2} = 165{,}000 \text{ Btu}$$

$$U = 100 \text{ Btu/hr-°F-ft}^2$$

$$\Delta t = 30°$$

$$A = \frac{165{,}000}{100 \times 30} = 55 \text{ ft}^2$$

CONDENSER

9# min x 60 = 540#/hr steam
400#/hr EDC

$$Q = 540 \times 970 + 400 \times 137 = 580{,}000 \text{ Btu/hr}$$

$$U = 200 \text{ Btu/hr - °F - ft}^2$$

$$\Delta t = 75°F$$

$$A = \frac{580{,}000 \text{ Btu/hr}}{200 \times 75} = 39 \text{ ft}^2$$

STEAM CONSUMPTION

540#/hr to stripper

and $\frac{165{,}000 \text{ Btu/hr}}{970 \text{ Btu/\#}} = 170\#/hr$ to heater

Total Steam = 710#/hr

OIL CARRY OVER:

at 230°F, $K_{oil} = .017$

Moles (EDC + H_2O) = 0.567 moles/min

$$\text{Moles oil/min} = 0.567 \times \frac{0.017}{0.983} \approx 0.01 \text{ moles/min}$$

This is 1.84#/min of oil.

This would have only slight effect on previous calculations but would require a small evaporator to remove the EDC from the oil and perhaps another 60#/hr of steam.

THE SIGNIFICANT EQUIPMENT LIST IS

5 1/2' x 23' agitated extractor
36' stripper
300 ft^2 heat exchanger
55 ft^2 heater
39 ft^2 condenser
two 20 GPM oil pumps
one 100 GPM water pump
Oil surge tank, about 200 gal.
6,000 gal. feed tank
50 gal, decanter

The purchase costs of the major items of equipment are shown in TABLE 4. The total capital investment would be about 4 times as large. So we have a total capital investment of perhaps $400,000 and a steam consumption of about 700 lb/hr.

TABLE 4

Purchase Cost of Major Items of Equipment for Extraction System (1973)

	Extraction System	
	Stainless	Carbon Steel
Extractor	68,000	68,000 (ss)
Heat exchanger	9,000	3,600
Heater	3,700	1,600
Condenser	3,000	2,500
Pumps & Motors	3,800	2,500
Stripper	14,000	5,600
Tanks	13,300	5,500
TOTAL	114,800	89,300

SECTION 7

DESIGN OF PROCESS FOR REMOVAL OF CHLORINATED-SOLVENTS FROM WASTE STREAMS BY STEAM STRIPPING

(A comparison of solvent extraction and stripping)

Though this report is concerned with solvent extraction, nearly all of the chlorinated solvents for which extraction data are given in Table 1 can also be removed by stream stripping. Since stripping is inherently a simple operation it seems pertinent to design stripping and extraction processes for the same components to get some measure of their relative process and economic advantage.

STRIPPER SYSTEM DESIGN

A schematic diagram of this system is shown in Figure 5. The following physical properties will be used:

$$C_p(H_2O) = 1 \text{ Btu/lb} - °F$$

$$\Delta H_v(H_2O) = 970 \text{ Btu/lb} = 17{,}500 \text{ Btu/mole}$$

$$\Delta H_v(EDC) = 137 \text{ Btu/lb} = 13{,}600 \text{ Btu/mole}$$

The mole fraction of EDC in the feed is 0.001465.

We do not have vapor liquid equilibrium data for the EDC-H_2O system. However, because of the low mutual solubility, it is possible to construct useful equilibrium data from solubility and vapor pressure data.

The solubility of EDC in water at temperatures to 70°C is shown in Figure 6. Vapor pressures for EDC and other substances are given in Figure 7. We are only interested in the vapor-liquid equilibrium for the water rich phase. Assuming that the saturated water phase is in equilibrium with pure EDC we may write, assuming Henry's law.

$$P^*_{EDC} = H.X_{EDC \cdot Sat.}$$

We want the Equilibrium Constant at 1 atm so dividing both sides by 1 atm we obtain

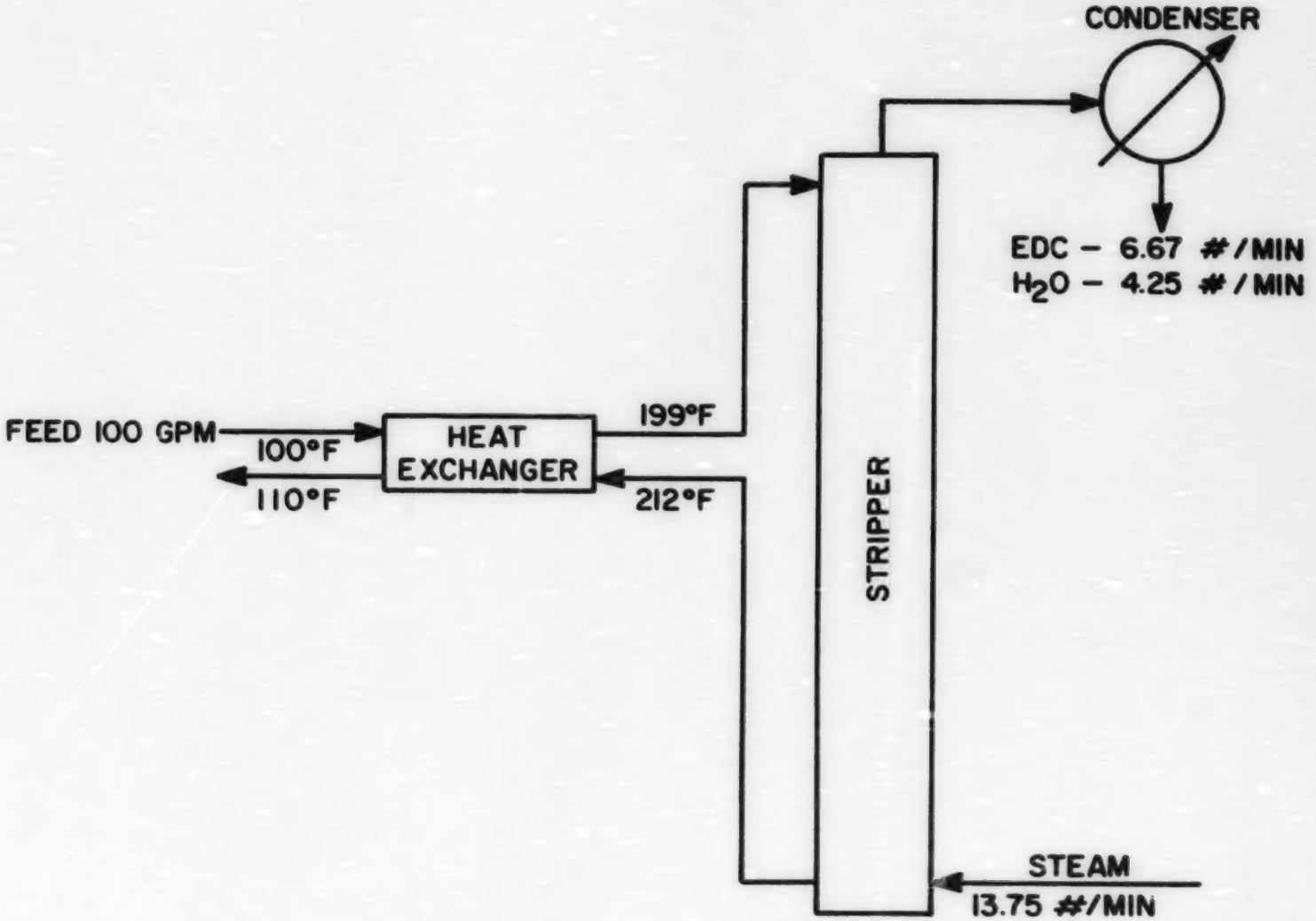

Figure 5. Steam stripping system.

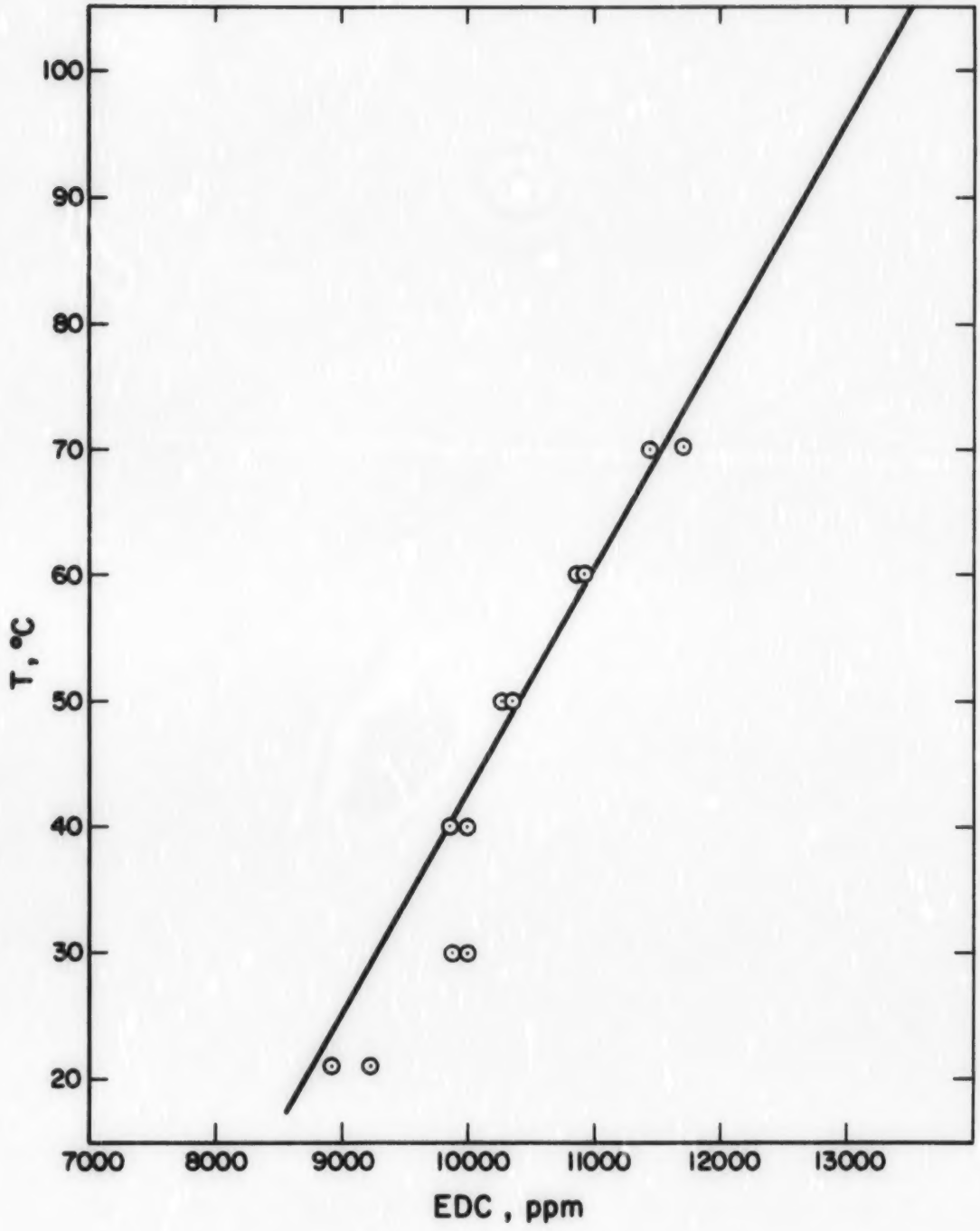

Figure 6. Solubility of EDC in water.

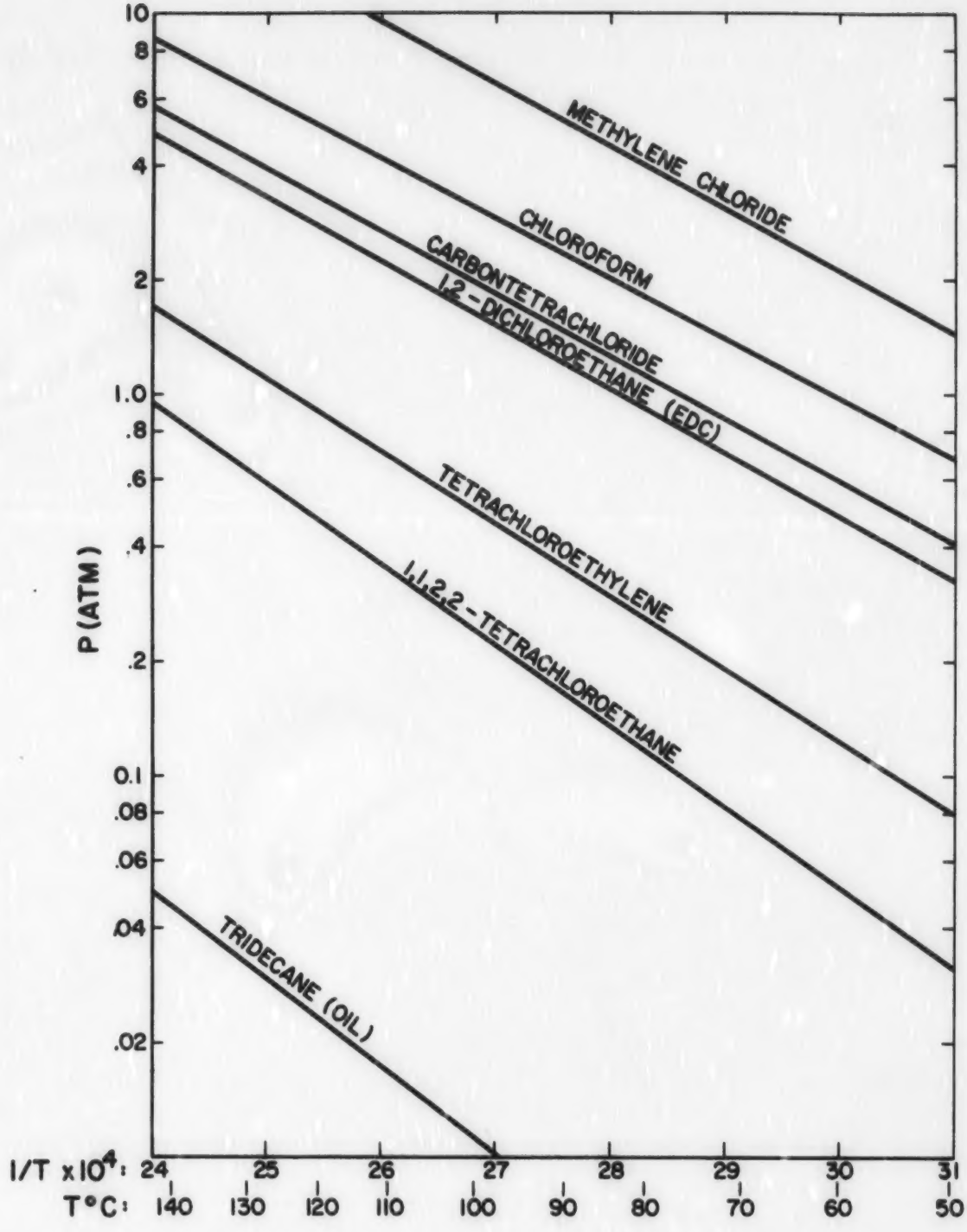

Figure 7. Vapor pressures of various substances.

$$Y_{EDC} = P^*/1 = (H/1)x = KX$$

$$K_{1atm} = P^*/X_{EDC \cdot Sat.}$$

where

P^* = Vapor pressure, atm

H = Henry's law constant, atm

$X_{EDC \cdot Sat.}$ = Mole fraction EDC at saturation

Y_{EDC} = Mole fraction EDC in vapor

K = Equilibrium constant, Y/X

Since the water phase is practically pure water, K for water at one atmosphere is equal to the vapor pressure in atmospheres.

Reading solubility from the extrapolated solubility seen in Figure 6 and vapor pressures from Figure 7 the equilibrium data in Figure 8 were calculated. Assume the stripped water leaves the stripper at 212° F and is cooled in the heat exchanger to 100°F. Assume the feed enters at 100°F. A heat balance will determine the temperature into the column.

Assume 199°F = 365.7°R

From Figure 8 we obtain K_{EDC} = 540, and K_{H_2O} = 0.74. A flash calculation on 1 mole of feed yields 0.000482 moles of EDC remaining in the feed and 0.000983 moles of EDC, and 0.0028 moles of H_2O flashed. A heat balance on a mole of feed gives

$$18(102) = 18(t-100) + 13{,}600 \times 0.00098 + 17{,}500 \times 0.0028$$

t = 198.5°F which is close

The maximum L/V ratio at the top of the column = 540. Take an actual value of 2/3 this to obtain L/V = 360 = 0.00278 moles of vapor. The total vapor leaving the top of the column is the sum of this plus the flashed vapor or 0.00656 moles per mole of feed. Since essentially all the EDC has been stripped, this vapor contains 0.00146 moles of EDC and 0.0051 moles of water.

An overall heat balance can now yield the amount of steam entering. The heat leaving per mole by incomplete temperature approach in the heat exchanger is 18 x 10 = 180 Btu, so

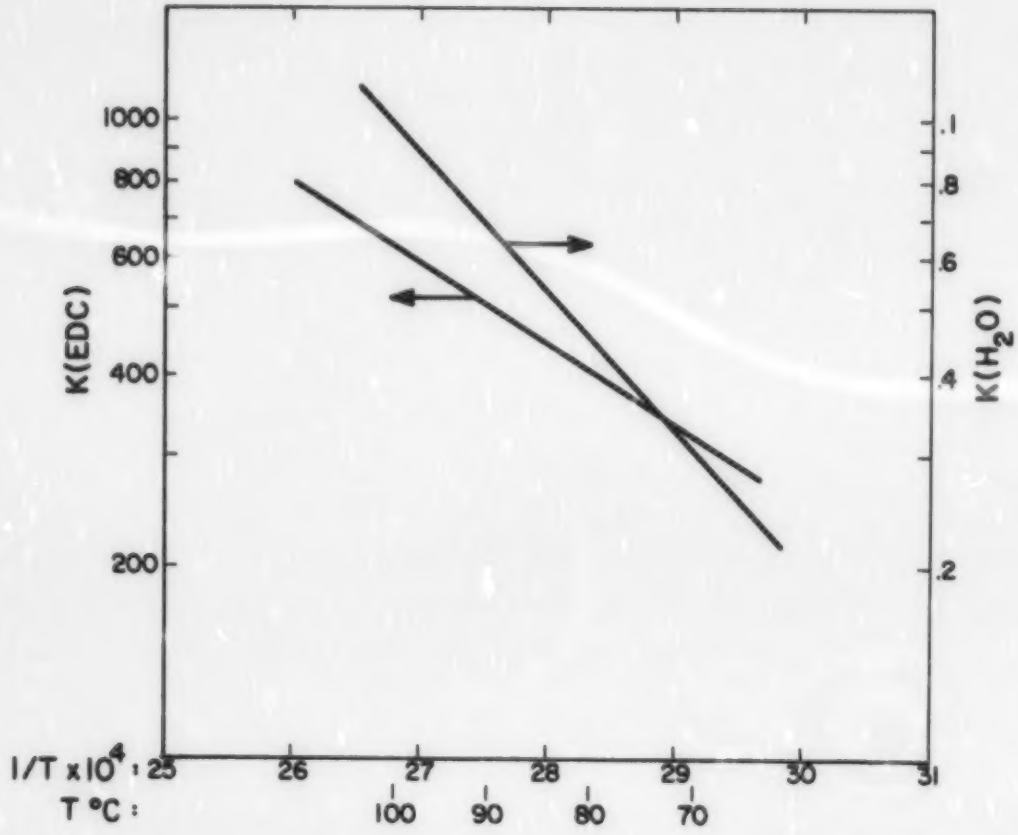

Figure 8. Vapor-liquid equilibrium constants for EDC and Water (Water Rich Phase) at 1 atm

$$180 = 17{,}500\,(V - 0.0051) - 13{,}600 \times 0.00146$$

$$V = 0.0165 \frac{\text{moles steam}}{\text{moles of feed}}$$

SIZING COLUMN

The equilibrium constants at top and bottom are

$$K_{TOP} = 540$$

$$K_{BOTTOM} = 640$$

$$V/L_{TOP} = 1/360 = .00278$$

$$V/L_{BOTTOM} = .0165$$

The stripping factors, KV/L, are

$$S_{TOP} = 540 \times 0.00278 = 1.5$$

$$S_{BOT} = 640 \times 0.0165 = 10.5$$

The mole fractions are

$$X_{TOP} \text{ (after flashing)} = 0.000482$$

$$X_{BOTTOM} = 15 \times 10^{-6} \times 18/99 = 0.0000027$$

for a ratio $X_{TOP}/X_{BOT} = 178$

Calculating the number of transfer units from S_{TOP} and S_{BOT} we have

$$N_{TOP} = 12$$

$$N_{BOT} = 5$$

Use $N = 9$ and $H_t = 2'$

Where N is the number of transfer units and H_t is the height of a transfer unit so the tower height = 18'. Add 6' for ends and distribution to obtain 24'.

Calculation of the column diameter was made using flooding charts of U.S. Stoneware and assuming 1" Intalox saddles. A flow rate of 70% of flood was assumed yielding a 2' column.

HEAT EXCHANGER

The heat transferred in the feed-bottom exchanger is given by

$$Q = 100 \frac{gal}{min} \times 60 \frac{min}{hr} \times 8.33 \frac{\#}{gal} \times 102°F = 5.1 \times 10^6 \frac{Btu}{hr}$$

$$U = 200 \text{ Btu/hr - °F - ft}^2$$

$$\Delta t = (10 + 13)/2 = 11.5°$$

$$A = \frac{5.1 \times 10^6}{200 \times 11.5} = 2220 \text{ft}^2$$

CONDENSER

$$\#EDC/hr = 400$$

$$\#H_2O/hr = 0.0051\#/\#Feed = 255\#/hr.$$

$$Q = 400 \times 127 + 255 \times 970 = 302{,}000 \text{ Btu/hr}$$

$$U = 200$$

$$\Delta t = 75°$$

$$A = \frac{302{,}000}{200 \times 75} = 20 \text{ ft}^2$$

Assuming the feed is available at sufficient pressure to enter the column, one 100 GPM pump is required for the column bottoms and a very small pump for the recovered EDC: The condensed steam could be allowed to flow by gravity back into the stripper feed pump suction.

THE SIGNIFICANT EQUIPMENT LIST BECOMES

2' x 18' packed column

2220 ft^2 heat exchanger

20 ft^2 condenser

2-100 GPM pump

6000 gal. feed tank

30 gal. decanter

The costs of the principal items of equipment are shown in TABLE 5. The total installed cost would be about four times this much but a comparison with the results in TABLE 4 indicates that stripping is clearly preferable The steam consumption is about the same and the equipment is at least 50% more for the extraction system. Since in the extractor system, the extractor cost is predominant and its diameter would only be slightly

reduced by reduced oil flow, it would appear that extraction would most likely compete with steam stripping only in systems of poor relative volatility.

TABLE 5

PURCHASE COST OF MAJOR ITEMS OF EQUIPMENT FOR STRIPPING SYSTEM (1973)

Stripping System (Stainless)	
Stripping Column	19,000
Heat exchanger	30,000
Condenser	2,000
Tanks	11,000
Pumps & Motors	2,000
	64,000

SECTION 7

PILOT PLANT DESIGN

We have designed a pilot plant to handle a mixture of volatile and less volatile chlorinated compounds in water using a paraffin hydrocarbon oil as the solvent. The design follows and is shown in Fig 9.

Feed rate = 1 GPM
Solvent rate = 0.2 GPM

Solvent Properties

Hydrocarbon paraffinic oil - approximately C_{12} - C_{13}

Viscosity at 1[illegible]°F = 2 Centipoise

Viscosity at 265°F = 0.6 Centipoise

Specific gravity = 0.76 - 0.78

Design Feed Composition:

Water Contaminated with:

Ethylenedichloride = 9,000 ppm
1,1,2,2 Tetrachloroethane = 500 ppm

EXTRACTOR DESIGN

On a volume basis

$$K_{EDC} = 15$$

$$K_{1,1,2,2} = 25$$

$$E_{EDC} = 3$$

$$E_{1,1,2,2} = 5$$

Based on constant oil to water ratio and distribution constant, the relation of these variables to the number of theoretical stages is given by

$$\frac{X_{N+1} - X_1}{X_{N+1} - X^*} = \frac{E^{N+1} - E}{E^{N+1} - 1}$$

where

$$k_v = \frac{\text{volume Concentration in Solvent}}{\text{volume Concentration in Water}}$$

$E = K_v L_{ov} / L_{wv}$

L_{ov} = Solvent flow rate, volume

L_{wv} = Feed water flow rate, volume

N = Number of stages

X_1 = Concentration of solute in water leaving extractor

X_{N+1} = Concentration of solute in water entering extractor

X^* = Concentration of solute in water in equilibrium with the stripped solvent

For EDC, with essentially no recycle in the oil solvent, the left-hand side is the fraction removed and is equal to 0.997 with 5 stages. For 1,1,2,2-tetrachloroethane we will essentially have equilibrium with the recycle oil and recovery depends on stripping efficiency.

Packed Column Extractor

Estimation of diameter based on U.S. Stoneware design charts indicates 7 1/2 - 8" with 1/2" Intalox saddles. The height is difficult to estimate. Probably between 3 and 5 feet per stage will be required giving, say 25 feet of packing.

It is our recommendation, however, that manufacturers of mechanically agitated equipment be contacted before an extractor is decided upon.

STRIPPER DESIGN

The Steam stripper is at one atmosphere with a Liquid/Vapor ratio of one on a mole basis.

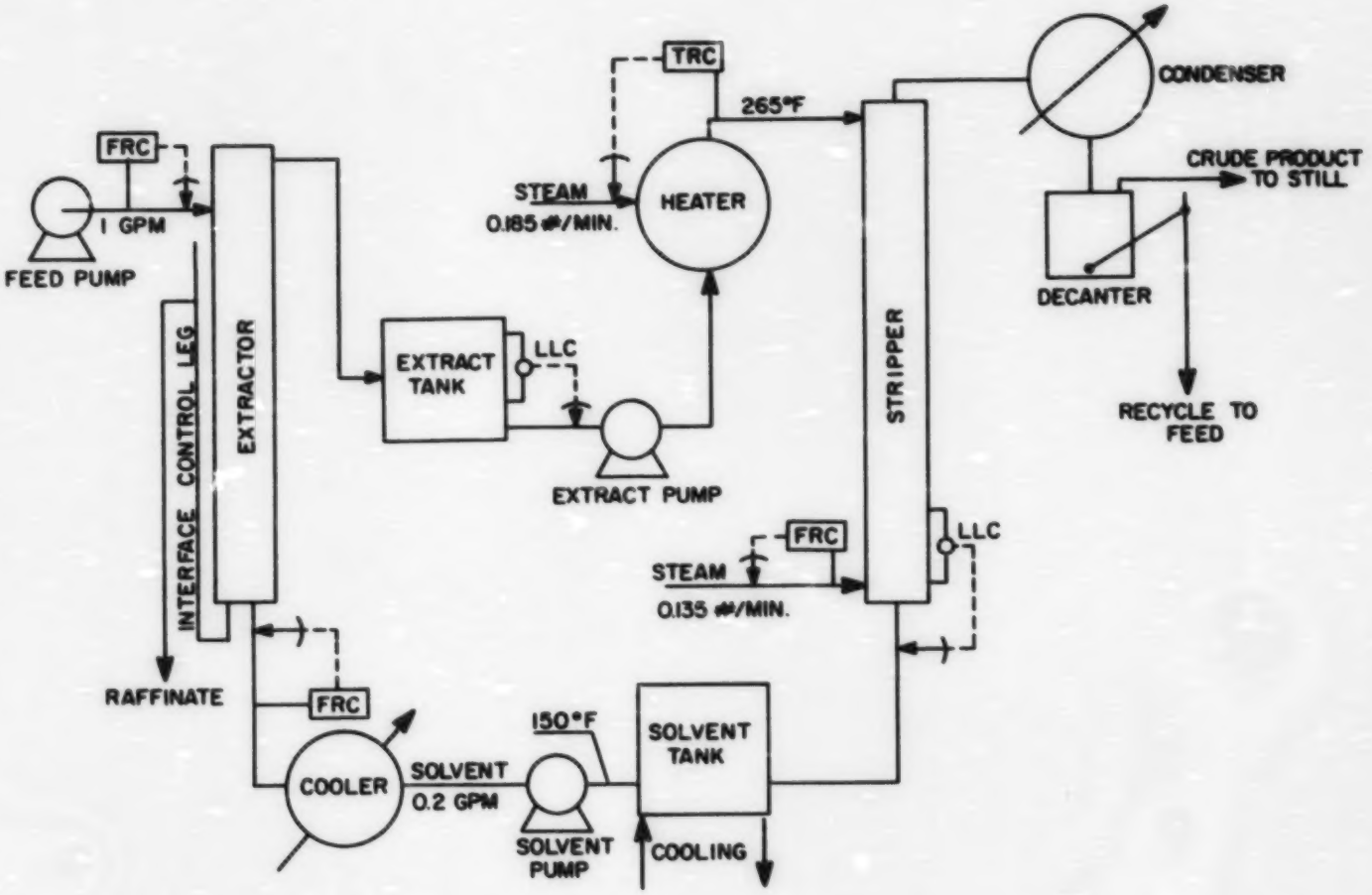

Figure 9. Pilot plant design

$$L = \frac{1.27\#/min}{170\#/mole} = .00747 \ \frac{moles\ oil}{min}$$

$$V = .00747 \ \frac{moles\ steam}{min} = 0.134 \ \frac{\#\ steam}{min}$$

at 265°F

$$K_{EDC} = 3.5$$

$$K_{1,1,2,2} = 1$$

$$K = \frac{mole\ fraction\ in\ vapor}{mole\ fraction\ in\ liquid}$$

The fraction solute removed is given by

$$fraction\ removed = \frac{S^{N+1} - S}{S^{N+1} - 1}$$

in which $S = \frac{VK}{L} = 3.5$

Assume 6 stages

This gives essentially all EDC stripped. For 1, 1, 2, 2, tetrachloethane the resultsfrom the above equation is indeterminate, but for this case the fraction removed is N/N+1 or 6/7.

Packed Column Stripper

Diameter = 3"
Packing 1/4' Intalox saddles
Height at least 8' with redistribution of liquid at several points

Calculation of Final Raffinate Concentration

Concentration of 1,1,2,2 remaining in oil

1/7 x 500 ppm in feed x 5/.76 wt. ratio $\frac{feed}{oil}$ = 470 ppm

Concentration in equilibrium with oil = $\frac{470}{25}$ = 19 ppm

fraction tetrachloroethane removed = $\frac{500 - 19}{500}$ = 0.963

EDC concentration remaining = 9,000 x 0.003 = 27 ppm

Pilot Plant Equipment

Figure 9 shows flow rate, temperatures where important, tank capacities, and controls.

Equipment Required

Feed Storage
Feed Pump - 1 GPM
Two Solvent Pumps - 0.20 GPM
Condenser - 1.5 sq. ft.
Steam Heater - 1 sq. ft. (assuming at least 50 psig steam)
Solvent Cooler - 5 sq. ft.
Solvent Tank - 20 gal.
Extract Tank - 5 gal.
Decanter - 5 gal.
Extractor
Stripper
Crude Product Still

Controls

Feed Flow Control
Solvent Flow Control
Stripper Steam Flow Control
Stripper Feed Temperature Control
Extract Tank Level Control
Stripper Level Control

Discussion of Design

Extractor — Though a packed column is specified, vender quotes for agitated towers should be obtained.

Crude Product Still — Not shown in this design is a crude product still. The overhead from the stripper will contain a high fraction of oil and some kind of recovery system might be desirable. This could be a batch operation.

Heat Exchangers — The condenser, cooler, and heater are so small that fabricated double-pipe design could be used. It might be asked why a Solvent-Extract exchanger is not specified. In the first place the system is too small to make heat recovery important, and secondly, with This exchanger the solvent pump would have to pump 265°F oil complicating the specifications of the pump.

Solvent Tank — This tank should contain about 20' of 1/2" tubing for cooling water which will drop the temperature below 150°F at which almost any kind of solvent pump can be used.

Extract Tank	This is strictly for surge capacity between the extractor and stripper.
Stripper	This unit is designed for feed containing some heavier components as represented by 1,1,2,2 tetrachloroethane. If not present, the stripper steam flow or temperature could be reduced.

SECTION 9

THERMODYNAMIC ANALYSIS OF EXTRACTION VS STRIPPING

OF VOLATILE DILUTE COMPONENTS

The following is an attempt to apply thermodynamic analysis to the case in which a volatile, dilute solute - and in particular the chlorinated hydrocarbons - is extracted by a nonvolatile solvent from water.

We will assume that the solute in water obeys Henry's law

$$p = HX.$$

where

p = partial pressure, atm
H = Henry's Constant, atm
X = mole fraction

As discussed earlier, at saturation we may assume the dilute solution in water to be in equilibrium with pure solvent, so p, the partial pressure, is equal to P* the vapor pressure.

$$P^* = HX_{sat}.$$

or dividing by the total pressure Π

$$\frac{p}{\Pi} = Y = \left(\frac{H}{\Pi}\right) X_{sat} = K_g X_{sat}$$

or the equilibrium constant for vapor-liquid equilibrium is

$$K_g = \frac{P^*}{\Pi X_{sat}}$$

Where $K_g = Y/X$ = Vapor mole fraction/liquid mole fraction.

We will assume that the solute deviation from Raoult's law in the solvent phase can be expressed by

$$p = P^* \gamma X$$

where γ is the activity coefficient.

$$\frac{p}{\Pi} = y = \frac{P^* \gamma X}{\Pi} = K X$$

In the solvent phase

$$K_g = \frac{P^* \gamma}{\Pi}$$

For liquid-liquid equilibrium, the partial pressures are equal in each phase, so Y in equilibrium with each phase is the same

$$Y = \frac{P \gamma X_o}{\Pi} = \left(\frac{p}{\Pi X_{sat}}\right) X_w$$

or

$$\frac{X_o}{X_w} = K_L = \frac{1}{\gamma X_{sat}}$$

where X_o and X_w are the mole fractions in the oil (assuming an oil solvent) and water phase respectively. This is true for any slightly soluble component and should apply to the extraction of all the chlorinated hydrocarbons studied in section IV.

The ease of extraction is given by the extraction factor

$$E = \frac{K_L L_o}{L_w}$$

The ease of stripping is measured by the stripping factor

$$S_w = \frac{K_{gw} V_w}{L_w}$$

The ease of solvent recovery is given by

$$S_o = \frac{K_{go} V_o}{L_o}$$

where

K_L = Liquid-liquid equilibrium constant

K_{gw}=Vapor-liquid equilibrium constant in the water stripper

K_{go} = Vapor-liquid equilibrium constant in the oil or solvent stripper

L_o, L_w = Oil and water flow rates in moles per unit time

V_w = Steam rate in the water stripper, moles per unit time

V_o = Steam rate in the oil stripper, moles per unit time

Substituting the definitions of K

$$E = \frac{L_o}{\gamma_E X_{sat,E} L_w}$$

$$S_w = \frac{P^*_w \ V_w}{\pi X_{sat,w} \ L_w}$$

$$S_o = \frac{P^*_o \gamma_o V_o}{\pi \ L_o}$$

where $X_{sat,E}$ is the mole fraction of EDC in water at saturation in the extractor, $X_{sat,w}$ is the mole fraction of EDC in water at saturation in the water stripper, and P^*_w and P^*_o are the vapor pressures of EDC at the temperature of the water and oil stripper respectively.

We see from the cost analysis of stripping vs. extraction that S_w and S_o are at least the same order of magnitude. For simplification let us equate them.

$$\frac{P^*_w \ V_w}{X_{sat,w} L_w} = \frac{P^*_o \ \gamma_o \ V_o}{L_o}$$

reorganizing and substituting,

$$\frac{P^*_w \ V_w E \ \gamma_E X_{sat,E}}{X_{sat,w}} = P_o \gamma_o V_o$$

$$E = \left(\frac{P_o^*}{P_w^*}\right)\left(\frac{X_{sat,w}}{X_{sat,E}}\right)\left(\frac{V_o}{V_w}\right)\left(\frac{\gamma_o}{\gamma_E}\right)$$

Since the cost estimate indicates the extractor is the major cost, E should be large so

$$E = \left(\frac{P_o^*}{P_w^*}\right)\left(\frac{X_{sat,w}}{X_{sat,E}}\right)\left(\frac{V_o}{V_w}\right)\left(\frac{\gamma_o}{\gamma_w}\right) >> 1$$

but

$$\frac{P_o^*}{P_w^*} > 1$$

perhaps as much as 2 or 3 by running up the oil stripper temperature

$$\frac{X_{sat,w}}{X_{sat,E}} \sim 1.5 \text{ according to EDC data}$$

$$\frac{\gamma_o}{\gamma_E} < 1 \text{ perhaps as low as } 1/2$$

$$\frac{V_o}{V_w} \sim 1 \text{ or less}$$

One sees that we cannot have a large E unless we allow

$$S_o << S_w$$

which would run up the cost of the oil stripper.

The problem may be summarized as follows:both extractor and stripper efficiency are inversely proportional to solubility,

$$E \sim 1/X_{sat,E}$$

$$K_g w \sim 1/X_{sat,w}$$

Similarly both steam stripping and solvent recovery stripping are proportional to the vapor pressure

$$K_{gw} \sim P^*_w$$

$$K_{go} \sim P^*_o$$

While P^*_o can be greater than P^*_w and $X_{sat,E}$ is a little larger than $x_{sat,w}$, this is partly offset by $\gamma_o < \gamma_E$. This plus the fact that extractors tend to be larger and more expensive than strippers makes it unlikely that these relatively small ratios will allow extraction to best stripping in these systems.

To check the basic assumptions, let us calculate K for EDC and compare it with the experimental value.

The activity coefficient of the oil-EDC system should agree fairly well with the theory of Hildebrand (9) in which the activity coefficient at infinite dilution is given by

$$\ln\gamma_2 = \left(1 - \frac{V_2}{V_1}\right) + \frac{V_2(\delta_2-\delta_1)^2}{RT}$$

$$V = \frac{MW}{\rho}$$

where

V = Molar volume, cm^3
δ = Hildebrand's solubility parameter
MW = molecular weight
ρ = density, gm/cm^3

$$V_{EDC} = \frac{99}{1.246} = 79.5$$

$$V_{oil} = \frac{184}{.79} = 233$$

$$\ln\gamma = \left(1 - \frac{79.5}{233}\right) + \frac{79.5(9.9 - 7.8)^2}{600} = 1.225$$

$$\gamma_{EDC} = 3.4$$

This agrees generally with γ_{EDC} in oil calculated from vapor pressure measurements.

$$X_{sat,EDC} = 9000 \text{ pm}$$

on a mole basis.

$$X_{sat,\ EDC} = 9000 \times \frac{18}{99} \times 10^{-6} = 0.00164$$

$$K_L = \frac{1}{3.4 \times .00164} = 180$$

This is on a mole basis. To convert to a volume basis we have

$$K_L = K_{Lo}\ (\text{mole}) \times \frac{MW(H_2O)}{MW(\text{oil})} \frac{\rho\ (\text{oil})}{\rho\ (H_2O)}$$

$$K_L = \frac{180 \times 18 \times .79}{184 \times 1} \cong 14$$

This is a little below measured values.

In Table 6 the value of $\frac{1}{X_{sat.}}$, $P^*(100°C)$ and $P^*/X_{sat.}$, the factors that primarily determine the efficiency of extraction, solvent recovery, and stripping are given. In the table, we have ignored the difference in P^*_o and P^*_w and $X_{sat,w}$, since as shown, these factors are likely to cancel.

Considering the cost of the EDC extractor, we should look for a system with larger 1/X relative to P*/X. For perchloroethylene the solubility is so low that extraction or stripping can hardly be justified. The best system in Table 6 might be $C_2Cl_4H_2$, but note that the stripping factor for this compound is only slightly less than for EDC, and the low pressure would require a high oil stripper temperature, so even this system is marginal. Incidentally, if both EDC and 1,1,2,2-tetrachlorethane were present, the stripping system could handle it easily. With extraction, we would have a very difficult situation in that EDC would limit the extraction system and the heavy component would limit the solvent recovery system.

TABLE 6. EXTRACTION AND STRIPPING FACTORS

Solute	X_{sat}	P*(100°C)(atm)	$1/X_{sat}$	P^*/X_{sat}
CH_2Cl_2	0.00425	7	235	1,650
$CHCl_3$	0.0011	3.1	910	2,800
Cl_4	9.3×10^{-5}	2	11,000	21,000
$C_2Cl_2H_4$(EDC)	0.00164	1.6	610	1,000
$C_2Cl_4H_2$	0.0003	0.24	3,300	800
C_2Cl_4	1×10^{-5}	0.50	10^5	50,000

From this analysis it appears that there is little chance that solvent extraction can compete with stripping for recovery of chlorinated solvents from waste waters.

SECTION 10

OZONATION OF WASTE WATER STREAMS

It has been shown in earlier work (5, 6) that ozone is capable of destroying many refractory organic compounds in dilute water solutions. These data indicate that at low concentration, ozonation can be an economic tertiary treatment for producing high quality water. It was found that such variables as pH, temperature, and O_3/O_2 ratios were important in obtaining efficient ozonation.

The experiments reported here are of two kinds. First there is a batch system in which the water to be treated is placed in a 3ℓ flask and ozone containing oxygen is bubbled through it continuously and samples of water are withdrawn at time intervals for TOC analysis. Temperature is controlled by immersion of the flask in a constant temperature bath.

The second kind of experiment was run in the continuous ozonation system shown in Figure 10. This system consists of two reactors in series. Each reactor is a 4" pipe, 5' long. Feed water is introduced into the first reactor with a metering pump. The water in each reactor is circulated at the rate of 2-3 gal/min through an aspirator which also recirculates the gas in the reactor at a rate of about 10ℓ/min. The combined gas-liquid stream passes through a static mixer before re-entering the reactor. An ozone-oxygen stream, usually about 1ℓ/min containing 70-80 mgm/ℓ of ozone, is introduced into the first reactor as shown in Fig. 10 by means of a separate aspirator. Gas from the first reactor flows to the second reactor and out through a pressure regulator. Water from the first reactor overflows to the second. By using a 2 stage cocurrent flow, almost no ozone is present in the exiting gas.

RESULTS

Most of the ozone work was done on propylene glycol because two of the waste streams were of this type and because glycol in general has been found hard to treat. Figure 11 and Table 7 shows runs in the batch systems with dilute propylene glycol at three temperatures. These results are similar to those obtained with municipal wastes and various chemicals. The rate is accelerated by increase in temperature, and the reaction proceeds first order with respect to TOC concentration. The rate is less than that experienced with municipal wastes.

The industrial wastes are all of higher concentration, so a number of runs were made on water containing about 300 ppm of TOC in the form of

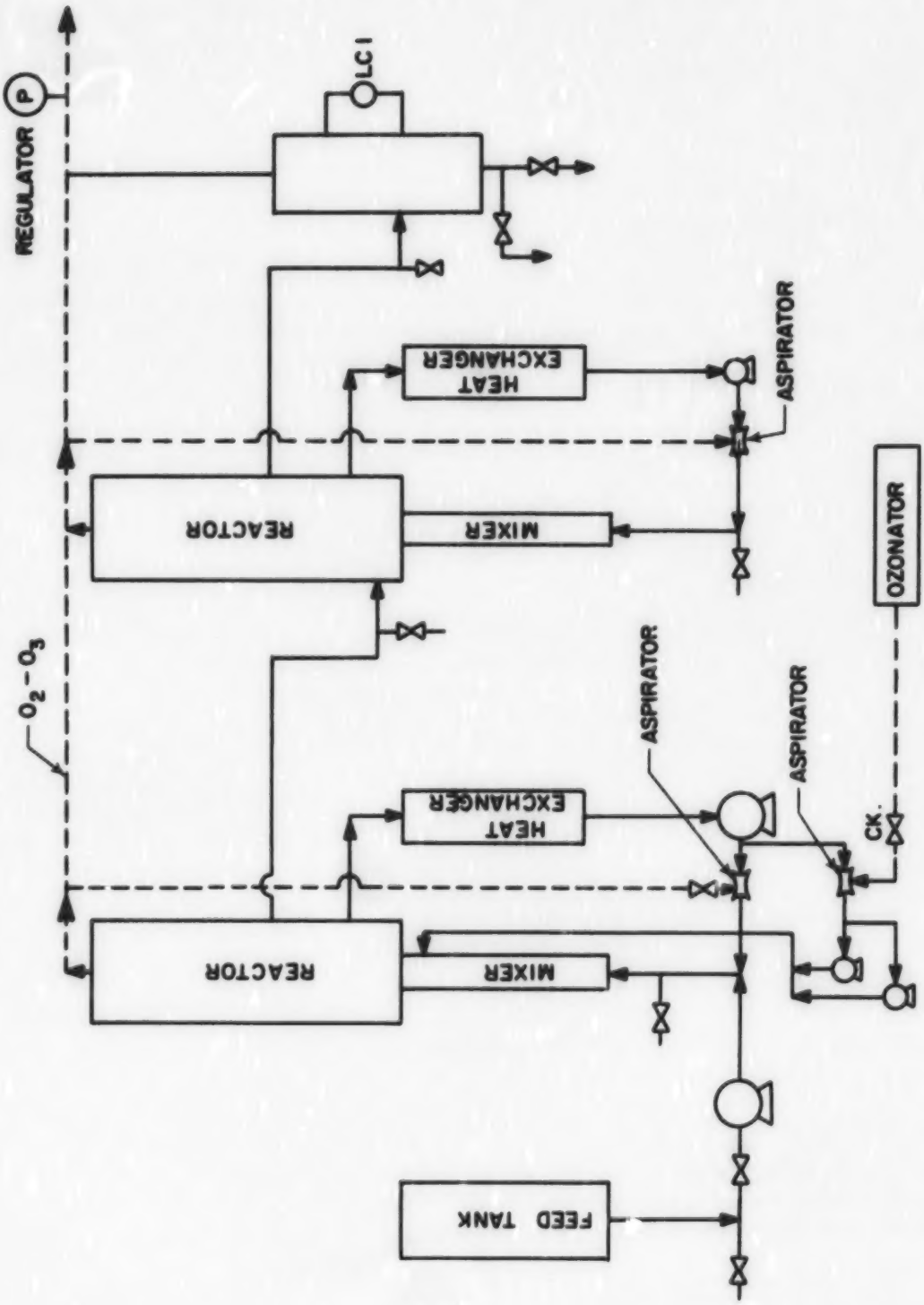

Figure 10. Continuous ozonation System.

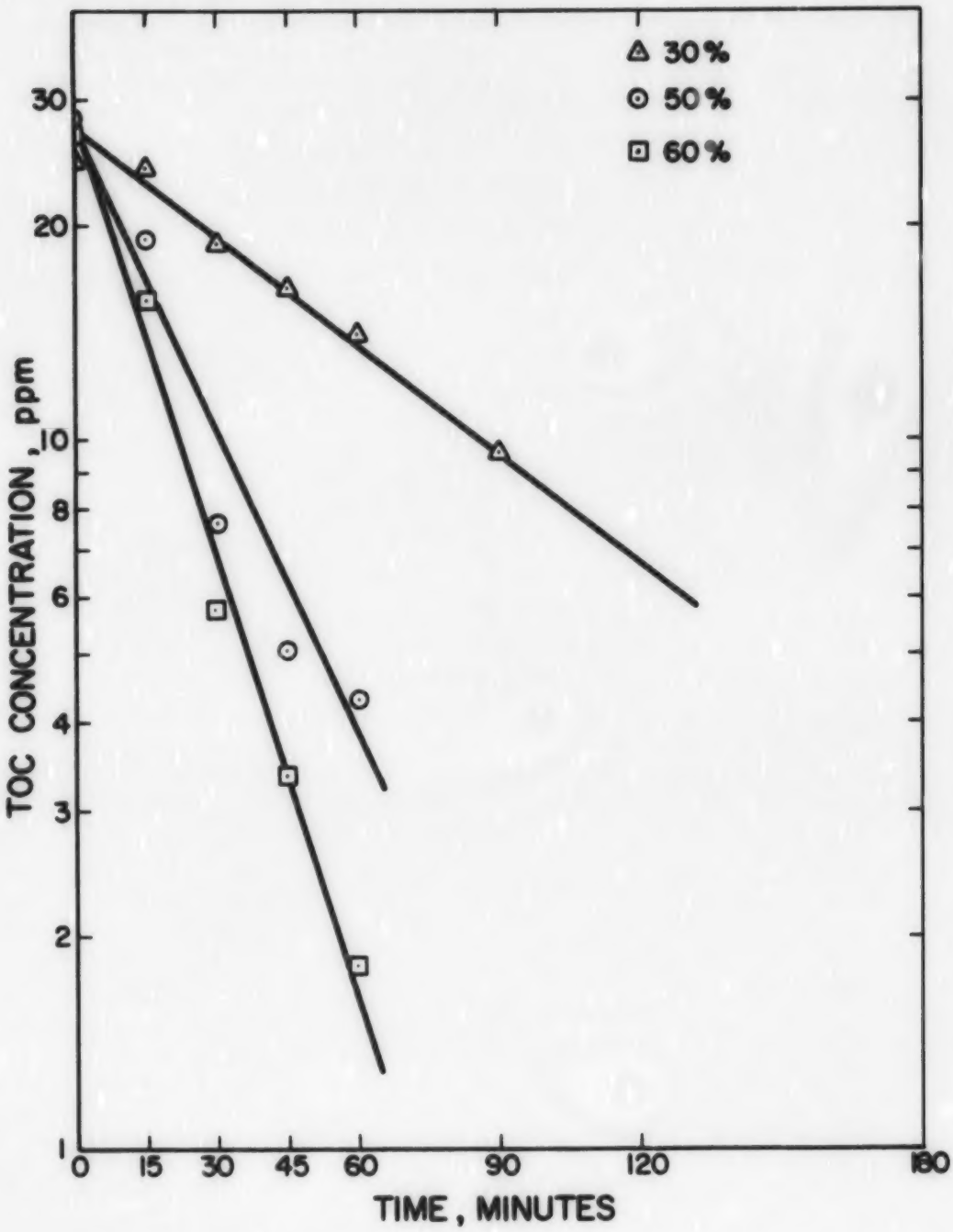

Figure 11. Ozonation of propylene glycol solutions.

propylene glycol, TABLE 8.

In runs with propylene glycol a rapid drop in pH was experienced, doubtless caused by the formation of organic acids. Various buffers were tried. $CaCl_2$ was used in the dilute data given in TABLE 7, but was unsatisfactory in the concentrated runs. In runs 18, 21 and 22 in TABLE

TABLE 7. OZONATION OF PROPYLENE GLYCOL
(dilute)

#11

Temperature : 50°C
Concentration : PG - 20.56 ppm
Buffer : $CaCl_2$

Time	pH	TOC
0	7.30	28.04
15	5.50	19.07
30	5.60	7.63
45	6.20	5.05
60	6.52	4.30
90	6.90	0.34
120	7.19	3.13
180	7.30	3.05
240	7.30	3.85

#12

Temperature : 60°C
Concentration : PG - 20.56 ppm
Buffer : $CaCl_2$

Time	pH	TOC
0	7.80	26.85
15	5.60	15.62
30	6.35	5.73
45	7.20	3.37
60	7.64	1.83
90	7.80	1.72
120	7.82	2.54
180	7.75	1.30

(continued)

#13

Temperature : 30°C
Concentration : PG - 20.56 ppm
Buffer : $CaCl_2$

Time	pH	TOC
0	8.01	24.22
15	6.00	24.01
30	5.41	18.78
45	5.55	16.33
60	5.68	13.93
90	5.80	9.51

TABLE 8. OZONATION OF PROPYLENE GLYCOL
(concentrated)

RUN #18 Temperature: 50°C
Concentration: PG - 436.7 ppm
Buffer: $NaHCO_3$ (2 gms)

Time	pH	TOC
0	8.55	334
15	8.75	280
30	8.75	289
45	8.60	293
60	8.50	290
90	8.38	308
120	8.30	288
180	8.40	190
240	8.90	31

RUN #21 Temperature: 60°C
Concentration: PG - 436.7 ppm
Buffer: $NaHCO_3$

Time	pH	TOC
0	8.6	273
30	8.5	247
60	8.5	261
90	8.6	242
120	8.6	204
150	8.7	136
180	8.9	54
210	9.2	34
240	9.4	29

RUN #22 Temperature: 50°C
Concentration: PG - 391.55
Buffer: None

Time	pH	TOC	ml of NaOh(n=0.0995)
0	8.0	322.8	0
30	3.5	315.0	9.1
60	3.5	304.2	17.5
90	3.5	304.8	21.7
120	4.3	287.3	14.45
150	5.1	274.2	4.9

Table 8 (continued).

#15

Temperature: 50°C
Concentration: PG - 413.6 ppm
Buffer: $CaCl_2$

Time	pH	TOC
0	8.00	347.0
15	4.35	329.1
30	3.70	326.0
45	3.55	323.2
60	3.60	311.7
90	3.85	280.0
120	4.22	249.6
180	4.85	174.9
240	6.90	42.5

8, $NaHCO_3$ was used. In all data on concentrated systems an unexplained phenomenon was encountered. There was a drop in TOC at the beginning. If the system was unbuffered the pH dropped radically, and it is known that ozonation is poor at low pH, then the TOC decreased very slowly even in buffered solutions. After about 1-1/2 hrs the TOC dropped rapidly. Run #22 is an attempt to measure the acid formation during ozonation by stopping the ozonation periodically and titrating the acid formed.

In this run,

$$\text{mil eq of base} - 67.65 \text{ ml} \times 0.0995N = 6.73$$

Assuming the acid comes from OH groups

$$6.73 \text{ mil eq OH} = 36 \left(\frac{\text{TOC}}{\text{mil eq PG}}\right) \left(\frac{1 \text{ eq PG}}{2 \text{ eq OH}}\right) \times \frac{6.73}{2\ell} = 60 \frac{\text{TOC}}{\ell}$$

That is, the TOC converted to acid is only slightly larger than the 48.6 mgm/ℓ of TOC that had disappeared, indicating that the conversion to acid is the limiting step.

Late in the project, the continuous unit described above became operational. Runs were made on dilute glycol solutions and the results are given in TABLE 9. Only pressure and flow were varied significantly in these runs and it is difficult to draw any certain conclusion.

We may calculate the efficiency of ozone using a typical run, #24, as follows:

$$\text{mgm TOC destroyed/min} = 0.150 \frac{\ell}{m} \times (36.3 - 23.2) \frac{\text{mgm TOC}}{\ell} = 1.91$$

$$\text{mgm } O_3 \text{ fed/min} = 1\ell \times 77.1 = 77.1 \text{ mgm } O_3\text{/min}$$

$$\frac{\text{mgm TOC destroyed}}{\text{mgm } O_3 \text{ fed}} \times 10 = \text{Efficiency}$$

$$\text{Eff} = \frac{1.97 \times 10}{77.1} = .255$$

The factor of 10 comes from the fact that only 1/3 of the oxygen in ozone is used and it takes 8 oxygens to destroy a molecule of propylene glycol, or 128 mgm oxygen to destroy 36 mgm of TOC. Thus it takes 3 x 128/36 or about ten. These results are much poorer than previous results for a variety of organic compounds (6) and it must be concluded that glycol is relatively refractory to ozone.

Batch Test on Toluene Diamine and Chlorinated Waste

The results of ozonating the toluene diamine waste is shown in TABLE 10. The same drop in pH was obtained as in the glycol runs. In view of this fact this waste was not tested further. It is noteworthy, however, that the dark color of this waste was destroyed very rapidly.

TABLE 9. CONTINUOUS OZONATION OF PROPYLENE GLYCOL STREAMS

(Gas Flow lℓ/min in all runs)

RUN #24

Reactors temperature: 51 C
Reactors pressure: 32 psig
Water feed rate: 150 ml per minute
Concentration of ozone in gas streams: mgm/ℓ
Gas stream in: 77.1
Gas stream out: 1.3
pH and concentration: TOC values in mgm/ℓ

	pH	TOC
Feed	7.15	36.3
Reactor 1	6.20	24.3
Reactor 2	6.90	23.2

RUN #25

Reactors temperature : 53 C
Reactors pressure : 30 psig
Water feed rate: 150 ml per minute
Concentration of ozone in gas streams: mgm/ℓ
Gas stream in: 77.2
Gas stream out: 0.8
pH and concentration: TOC values in mgm/ℓ

	pH	TOC
Feed	7.10	33.5
Reactor 1	6.30	23.4
Reactor 2	6.40	23.0

(continued)

RUN #27

Reactors temperature: 55°C
Reactors pressure : 12 psig
Water feed rate: 150 ml per minute
Concentration of ozone in gas streams: mgm/ℓ
Gas stream in: 77.0
Gas stream out: 0.9

pH and concentration: TOC values in mgm/ℓ

	pH	TOC
Feed	7.2	34.5
Reactor 1	6.2	23.5
Reactor 2	6.2	21.4

RUN # 28

Reactors temperature : 54°C
Reactors pressure: 0 psig
Water feed rate: 150 ml per minute
Concentration of ozone in gas streams: mgm/ℓ
Gas stream in: 77:0
Gas stream out: 1.7
pH and concentration: TOC values in mgm/ℓ

	pH	TOC
Feed	7.10	33.7
Reactor 1	6.45	28.7
Reactor 2	6.45	28.3

RUN #31

Reactors temperature: 52°C
Reactors pressure: 28 psig
Water feed rate: 75 ml per minute
Concentration of ozone in gas streams: mgm/ℓ
Gas stream in: 76.8
Gas stream out: 0.2
pH and concentration: TOC values in mgm/ℓ

	pH	TOC
Feed	7.10	17.42
Reactor 1	6.60	16.63
Reactor 2	6.40	13.99

TABLE 10. OZONATION OF TOLUENE DIAMINE

Temperature: 50°C
Concentration: TDA - 170 ppm
Buffer: none

Time (min)	pH	TOC	
0	7.85	415.8	(dark color)
30	3.03	318.0	(color gone)
60	3.28	284.6	
90	3.20	264.2	
120	3.10	245.7	
150	3.11	234.9	
180	3.20	219.0	
210	3.20	211.2	
240	3.20	204.7	

A similar test was run on sample O11A high in EDC. This is a high pH sample and the pH remained high through the run. Probably the pH was too high for efficient ozonation. The sample was first stripped with oxygen for an hour to remove volatiles and then ozonated with very poor results as seen in TABLE 11.

The rather uniformly poor results obtained with ozone was due to an unfortunate choice of wastes. Glycol turned out to be unusually refractory and nearly all the wastes were too high in TOC for effective ozonation. It has been demonstrated that many chemicals can be efficiently destroyed in dilute solution. Ozone has promise as a tertiary treatment to make either high quality water or to destroy small quantities of some refractory compounds.

TABLE 11. OZONATION OF CHLORINATED WASTE (SAMPLE O11A)

O_2 stripping - 50°C

Time (min)	TOC, ppm	pH
0	652.6	11.6
15	580.9	11.7
30	553.3	11.8
45	551.9	11.8
60	547.8	11.9

O_3 reaction - 50° C

Time (min)	TOC,ppm	pH
0	531.2	11.4
15	532.3 (?)	11.3
30	530.7	11.3
45	529.6	11.2
60	528.9	11.2
75	528.0	11.2
90	527.1	11.2
120	526.0	11.2

SECTION 11

CHEMICAL ANALYSIS

The concentration of ozone in all gas streams was measured iodo-metrically. A metered gas stream was bubbled through a porous disperser tube into 500 milliliters of 4% potassium iodide solution. The iodide solution was acidified and titrated with 0.05N sodium thiosulfate with starch as the indicator. The end point was detected by a color change, the color going from blue-black to clear.

The total organic carbon content of the waste water was determined with a Beckman Model 915 Total Organic Carbon Analyzer. The analyzer does rapid analyses of microsamples of waste water solutions for determining the total organic carbon content. The analysis actually consisted of two analyses which were performed on an identical sample. The total organic carbon content was the difference between the two obtained values for the analyses. The first analysis was the total carbon which consisted of organic carbon plus carbon in carbonates. The second analysis was the inorganic carbon which consisted of carbon in carbonates. Both analyses were based on the conversion of sample carbon into carbon dioxide for measurement by a non-dispersive infrared analyzer.

The individual chlorinated hydrocarbons content were determined with a Varian Aerograph Hy-Fi Model 600-D gas chromatography. The 5' x 1/8" stainless steel analytical column which was used with a hydrogen flame ionization detector was packed with 20% Silicone DC 550 on Chromosorb P. The injection temperature was 105°C while the oven temperature was from 100° to 150°C. Helium was used as the carrier gas in the gas chromatography. A Soltec recorder with a disc integrator was used to measure the amount of chlorinated hydrocarbon.

Many of the wastes contained hydrochloric acid which damaged the chromatography. For this reason TOC Analysis was relied on where possible. We discovered, however, that the ratio of TOC/GC was not theoretical. Fig. 12 shows the deviation of theoretical and actual TOC values for EDC in distilled water. Many of the industrial samples showed great deviations even from this graph. For instance in sample 011A, extraction of over 3000 ppm of EDC only reduced the TOC by about 250.

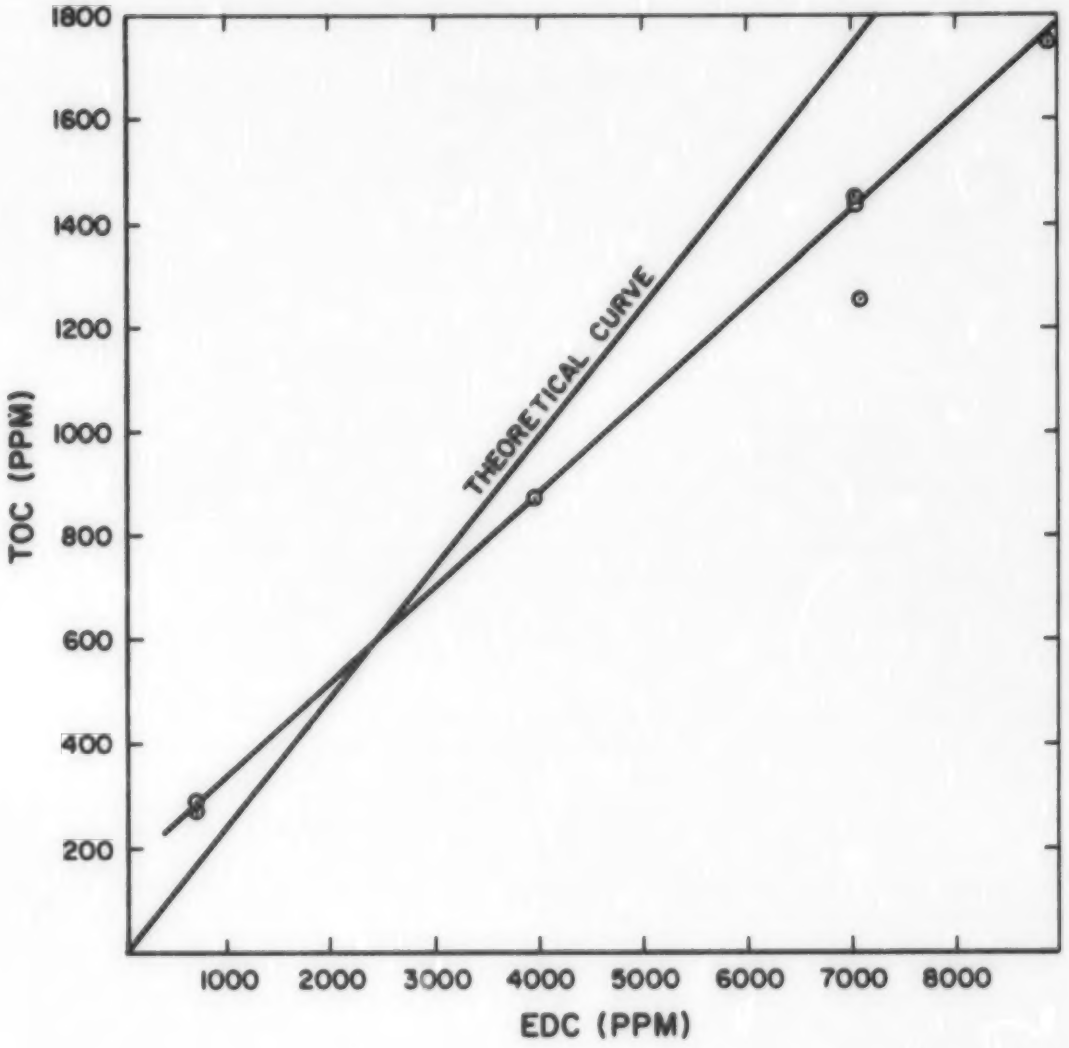

Figure 12. Theoretical vs actual TOC values for EDC.